

LOW TEMPERATURE SINTERING OF NICKEL FERRITE POWDERS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an improved process for sintering nickel ferrite powder, more particularly to including a mineralizer in the nickel ferrite powder which allows for reduced sintering temperatures to achieve high densification of the powder into a shaped component.

Prior Art

[0002] Conventional production of aluminum by the Hall-Heroult process involves electrolysis of alumina dissolved in molten salts of aluminum fluoride and sodium fluoride using carbon anodes. The anodes are suspended in a bath of the electrolytic fluid. Electric current supplied to the anodes results in production of electrons for reducing the alumina to aluminum which accumulates as a molten aluminum pad. The molten aluminum pad acts as a liquid metal cathode. During this process, the carbon anodes continually react with oxygen released during the reduction of alumina to produce CO₂ thereby decomposing and consuming the anodes. In view of the consumption of carbon, there have been attempts to produce non-consumable material for the anodes that would be resistant to oxidation and attack by the molten salt bath. Replacement of carbon anodes with inert anodes should provide a highly productive cell design and reduce capital costs. Significant environmental benefits are also possible because inert anodes do not produce CO₂ or CF₄ emissions. The use of a dimensionally stable inert anode also allows for efficient cell designs with a shorter anode-cathode distance and consequent energy savings.

[0003] The most significant challenge to the commercialization of inert anode technology is the anode material. The anode material must withstand the harsh environment of the Hall cell. In particular, the material should not react with or dissolve to any significant extent in the electrolyte bath. It must not react with oxygen or corrode in an oxygen-containing atmosphere and should be thermally stable at temperatures of about 1000° C. The anode material should have good mechanical strength and high electrical conductivity at the smelting cell operating temperature, about 950-970° C, so that the voltage drop at the anode is low. In addition,

aluminum produced with the inert anodes should not be contaminated with constituents of the anode material to any appreciable extent and the anode material should be relatively inexpensive.

[0004] Inert anodes formulated from nickel oxide (NiO) and iron oxide (Fe₂O₃) have found some success in electrolysis of alumina. These anodes are typically manufactured by blending powders of the metal oxides, calcining the mixture followed by grinding to a fine particle size. The fine particles are blended with organic binders and/or dispersants and formed into an anode shape. Once the component is formed in its “green” state, it is fired at temperatures typically at about 1350° C or higher in air or reduced oxygen atmospheres. During the firing process, the binder decomposes by oxidation or pyrolysis. At temperatures above 600° C, the particles of iron oxide and nickel oxide react and fuse together to form nickel ferrite. It has been found that sintering at temperatures well above 1200° C, such as over about 1400° C, is needed to maximize densification of the anodes.

[0005] High densification of the nickel ferrite anode is required to reduce the surface area of the anode and thereby minimize the opportunity for corrosion on the surface and within the anode. Full densification may be achieved at 1500° C, however significant energy input is required to achieve such high temperatures. In addition, the thermal energy which is stored in the anode following high temperature sintering creates thermal stresses within the anode that can result in failure of the anode. It has also been found that nickel ferrite anodes sintered at about 1500° C to achieve full densification contain relatively large grains at the surface of the anode. However, in the interior of the anode, the grain sizes are significantly reduced with concomitant higher quantities of grain boundaries. Grain boundaries have different chemistry from the bulk component and provide a route for the electrolyte bath and the alumina to enter the anode and effect corrosion. In addition, an anode suspended in an electrolyte bath has a portion which is normally outside of the bath and exposed to air. The interaction between air and the nickel ferrite anode also tends to create non-uniform grain sizes that compound the thermal stresses in the anode.

[0006] One objective of the present invention is to reduce the sintering temperature required to achieve full densification of nickel ferrite anodes. At lower sintering temperatures, the thermal stresses in the sintered anodes are lower and the anodes are more mechanically stable. A related need is to control the grain size in nickel ferrite anodes to be more uniform throughout the anodes with minimal grain boundaries.

SUMMARY OF THE INVENTION

[0007] This need is met by the method of the present invention of producing a sintered nickel ferrite component in which particles of iron oxide and nickel oxide are blended with an alkaline metal borate mineralizer. The mixture is shaped into a green compact. The green compact is sintered at temperatures less than about 1400° C. It has been found that use of an alkaline metal borate mineralizer allows for sufficient densification at temperatures less than 1400° C with larger grain sizes and greater uniformity through the thickness of the sintered component as compared to components produced according to the prior art. The alkali metal borate may be sodium borate, lithium borate or cesium borate. In some instances it may be helpful to use incipient wetting of the iron oxide particles by mixing the alkaline metal borate in an aqueous solution with the particles. A binder may be mixed with the particles to strengthen the green compact prior to sintering. The compact may include about 50 to 75 wt.% iron oxide and about 25 to 50 wt.% nickel oxide with sufficient concentration of the mineralizer to include about 0.025 to 1.6 wt.% boron. The present invention is particularly suited for producing an inert anode for use in electrolysis of alumina.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figs. 1a-1d is a set of micrographs of a nickel ferrite component produced according to the prior art;

[0009] Figs. 2a-2d is a set of micrographs of a nickel ferrite component produced according to the present invention using a lithium borate mineralizer;

[0010] Figs. 3a-3d is a set of micrographs of a nickel ferrite component produced according to the present invention using a sodium borate mineralizer; and

[0011] Fig. 4 is a graph showing the change in normalized size of the nickel ferrite components versus sintering temperature of Figs. 1-3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The present invention provides a method for producing a non-consumable electrode suitable for use in the production of metals by electrolytic reduction of their oxides in a molten salt bath. The method provides a high densification of the electrode to achieve chemical inertness and good electrical conductivity with acceptable mechanical properties. Inert electrodes produced according to the present invention are suitable for producing metals such as

aluminum, lead, magnesium, zinc, zirconium, titanium, lithium, thallium, silicon and the like, generally by electrolytic reduction of an oxide or other salt of the metal. When referring to any numerical range of values, such ranges are understood to include each and every number and/or fraction between the stated range minimum and maximum.

[0013] In the present invention, powders of NiO and Fe_2O_3 are blended in a mixer. The relative composition of iron oxide and nickel oxide in the mixture may vary such as about 50 to 75 wt.% iron oxide and 25 to 50 wt.% nickel oxide. The blended powders may be ground to a smaller particle size before being transferred to a furnace where they are calcined, typically for about 12 hours at about 1250°C . The calcination produces a mixture having nickel ferrite spinel and NiO phases. The calcined mixture is blended with a mineralizer of an alkali metal borate. The mixture of mineralizer and metal oxides is ground in a ball mill or the like to an average particle size of approximately 10 microns.

[0014] The fine particles may be blended with a polymeric binder, dispersants and water to make a slurry in a spray dryer. In an alternative embodiment, the alkali metal borate is added to the metal oxide powder mixture along with the binder instead of prior to the grinding step. The polymeric binder added to the mixture is preferably an organic material such as polyvinyl alcohol, acrylic acid polymers, glycol such as polyethylene glycol and a polyvinyl acetate, polyisobutylenes, polycarbonates, polystyrenes, polyacrylates and mixtures and copolymers thereof. The dispersants may also be organic materials. When used, about 0.1-10 parts by weight of the organics (binder and dispersant) are added to 100 parts by weight of the metal oxides. Preferably, about 3-6 parts by weight of the organics are added to 100 parts by weight of the metal oxides. The slurry typically contains about 60 wt.% solids and about 40 wt.% water. Spray drying the slurry produces dry agglomerates that are transferred to a V-blender for final mixing.

[0015] The V-blended mixture is isostatically pressed, for example at 20,000 psi, into anode shapes. The pressed shapes are sintered in air in a furnace heated to a temperature of less than about 1400°C for about 2-4 hours. The sintering temperature may be less than about 1200°C . The sintering furnace preferably contains an air atmosphere, but reduced oxygen or inert (e.g. argon) atmospheres may also be used. The sintering process burns out the polymeric binder from the anode shapes and achieves sufficient densification of the anode.

[0016] The alkali metal borate mineralizer is believed to facilitate transfer of material from high energy to low energy sites. Crystal growth during sintering is affected by particle characteristics, temperature, atmosphere, type of mineralizer and amount of mineralizer present. Alkaline metal borate compounds have been found to be suitable mineralizers for use in the present invention. In particular, borate compounds of sodium, lithium and cesium are suited for use in the present invention. Anhydrous alkaline metal borates are preferred over hydrous borates having a water constituent that increases the volume of material which is lost during densification. Very low amounts of mineralizer have been found to be effective in achieving low temperature sintering of nickel ferrite components. For example, the amount of boron from the mineralizer may be about 0.025–1.6 parts by weight boron, preferably 0.045-0.3 parts by weight boron, per 100 parts by weight of the metal oxides. Higher boron levels may be used without a deleterious effect. At such low amounts of mineralizer, it may be helpful to use incipient wetting to mix the mineralizer with the metal oxides or metal oxide/binder mixture. As such, the alkaline metal borate is presented in an aqueous solution of 0.5 – 0.7 wt.% boron for mixing with the metal oxides.

[0017] While nickel and iron oxides are preferred compounds for producing an inert anode, other suitable compounds may be oxides of tin, zinc, lithium, zirconium, chromium or tantalum. Other suitable compounds of the metals include metal salts that are converted to oxides when exposed to oxygen and elevated temperatures include halides, carbonates, nitrates, sulfates and acetates.

[0018] Inert electrodes made in accordance with our invention are preferably inert anodes useful in electrolytic cells for metal production operated at temperatures in the range of about 750-1080° C. A particularly preferred cell operates at a temperature of about 900-980° C, preferably about 950-970° C. An electric current is passed between the inert anode and a cathode through a molten salt bath comprised of an electrolyte and an oxide of the metal to be collected. In a preferred cell for aluminum production, the electrolyte comprises aluminum fluoride and sodium fluoride and the metal oxide is alumina. The weight ratio of sodium fluoride to aluminum fluoride is about 0.7 to 1.25, preferably about 1.0 to 1.20. The electrolyte may also contain calcium fluoride and/or lithium fluoride.

[0019] Although the invention has been described generally above, the particular examples give additional illustration of the product and process steps typical of the present invention.

EXAMPLES

Example 1: Comparative

[0020] A mixture containing 68.2 wt.% Fe_2O_3 , 29.8 wt.% NiO and 2 wt.% mixture of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) binders was pressed into a compact and sintered in air at 1500° C for two hours. Figs. 1A and 1B are photomicrographs of the resultant component after polishing near its edge and in the bulk of the component, respectively. Figs. 1C and 1D are photomicrographs of the component after thermal etching near the edge and in the bulk, respectively. It can be seen that away from the edge area, the grain sizes are significantly reduced with increased quantity of grain boundaries.

Example 2

[0021] A mixture of 68.2 wt.% Fe_2O_3 , 29.8 wt.% NiO, 2 wt.% mixture of PEG and PVA binders and 0.045 wt.% boron from lithium borate were pressed into a die to produce a green compact. The compact was sintered in air at 1200° C for two hours. Figs. 2A and 2B are photomicrographs of the resultant component as polished in the edge area and in the bulk of the component, respectively. Figs. 2C and 2D are photomicrographs of the component after thermal etching near the edge and in the bulk, respectively. It can be seen that the quantity of grain boundaries does not increase within the bulk of the component from the edge area and that the grain sizes are larger and more uniform than those produced in Example 1.

Example 3

[0022] Example 2 was repeated except that sodium borate was used in place of lithium borate. Figs. 3A and 3B are photomicrographs of the resultant component as polished in the edge area and in the bulk of the component, respectively. Figs. 3C and 3D are photomicrographs of the component after thermal etching near the edge and in the bulk, respectively. Again, uniformly sized large grains are present through the thickness of the component as compared to the component of Example 1.

[0023] In each of Examples 1-3, the change in size of the product was determined by dilatometry during the sintering process. A graph of the normalized change in dimensions versus sintering temperature is reproduced in Fig. 4. It will be appreciated that at temperatures over 900° C, greater densification occurred with the components produced according to the present invention using sodium borate and lithium borate as opposed to the control. At 1200° C, the components of the present invention were nearly fully densified, while the control component

was only about 60% densified. In addition, the electrodes produced according to examples 2 and 3 are believed to exhibit mechanical properties and electrical properties which were comparable to that of the control with improved chemical stability.